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(54) Diketone extraction

(57) A process for the extraction of a diketone, e.g. 'pongamol', comprises the steps of:

- i) extracting plant material obtained from *Pongamia sp.* or from *Tephrosia sp.* with an organic acid, and
- ii) separating a diketone from the acidic extract so obtained.

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METHOD OF EXTRACTIONFIELD OF THE INVENTION

This invention relates to extraction of natural substances from plant materials. The invention particularly relates to extraction of diketones useful for cosmetic applications, from certain plants of species like Pongamia glabra, P.pinnata, Tephrosia purpurea, T.Hamiltoni, T.flasiformis, T.Vogellii, T.lanceolata. The invention more particularly concerns a process for directly isolating "pongamol" [1,3-propanedione, 1-(4 methoxy-5-benzofuranyl)-3-phenyl] from the oil obtained from any part of the plant such as shell, bark, root, stem or seed. More specifically, the invention teaches a method of extraction of pongamol from commercial karanja oil, obtained from the seed by crushing, or by solvent extraction of the seed or cake.

BACKGROUND TO THE INVENTION AND PRIOR ART

Pongamol has been isolated from karanja oil by different methods such as molecular distillation of oil (N.V.Bringi, JOTA, (India), [1976], 8(3) 81) which required very high vacuum.

Other earlier researchers have isolated pongamol from karanja oil by a series of steps, usually involving separation from karanjin, followed by alcohol extraction of the oil and further purification.

5 In the process described in Ind.J.Pharm.[1941], 3, 3, and Proc. of Ind.Acad.Sci., [1942], 15A, 437, the karanja oil is first stored to remove karanjin and extracted with alcohol. The alcohol extract is stored  
10 and the separated material is taken up in ether and crystallised from ethanol-acetic acid.

15 In the process described in J.Ind.Chem.Soc., Industrial and News edition [1954], 17 39, dry hydrogen chloride is passed through the alcohol extract of karanja oil, the precipitate is separated and fractionally crystallised.

20 In the procedure described by R.N. Khanna and T.R. Seshadri in Tetrahedron [1963], 19, 223, the oily alcohol extract of the karanja oil, was stored in refrigerator (precipitated karanjin removed) and then chromatographed over alumina. From the light petroleum  
25 eluate, pongamol was isolated by countercurrent distribution between aqueous acetic acid and light petroleum.

30 The above procedure was modified by R. Aneja, R.N. Khanna and T. R. Seshadri (J.Chem.Soc., [1963], p.163) by eliminating the chromatographic step, but carrying out repeated partitioning of karanjin-removed-alcohol-extract between light petroleum and aqueous acetic acid.

35 We have surprisingly found that pongamol can be directly extracted from karanja oil, using

concentrated/dilute organic acid, like formic, acetic, propionic and butyric acid, for example, aqueous acetic acid.

5      DEFINITION OF THE INVENTION

Accordingly, the invention provides a process for the extraction of a diketone which comprises the steps of:

- 10      i)            extracting plant material obtained from Pongamia sp. or from Tephrosia sp. with an organic acid, and
- 15      ii)           separating a diketone from the acidic extract so obtained.

DESCRIPTION OF THE INVENTION

20      In accordance with the process of the invention, plant materials, especially the oils obtained from the shell, bark, root, stem or seed of Pongamia sp. or of Tephrosia sp. are extracted with an organic acid, and

25      diketones present in the extracts so obtained, are subsequently separated.

30      In accordance with a preferred embodiment of the invention, karanja oil is extracted using concentrated or dilute aqueous acetic acid in order to dissolve pongamol present in this starting material.

35      The extracts, after removal of the acid, are directly of use as enriched pongamol, or can be purified further by crystallisation from solvents, such as methanol or acetic acid.

Most preferably, pongamol can be directly obtained from karanja oil by extraction and in situ crystallisation with concentrated/dilute organic acid, ideally aqueous acetic acid, for example, 30 to 99% w/w, preferably 65 to 85% w/w acetic acid. The crystallisation can be carried out at a temperature of from 0 to 35°C, with or without the aid of conventional methods for accelerating crystallisation, such as seeding. Accordingly, karanja oil is stirred with aqueous organic acid at ambient temperature and the aqueous acid layer is separated and kept at ambient temperature to crystallise out pongamol, which is then filtered out and freed of adhering oil and acetic acid solution by washing with solvents, such as methanol and/or hexane.

According to another aspect of the invention, pongamol can be obtained from karanja oil settlings or split karanja oil fatty acids as well as from distilled fatty acid residues.

The invention is now described by way of example. The following example is intended to illustrate the invention and not to limit it.

EXAMPLES

Example 1

5           Karanja oil, commercial grade, Sangli Region, Acid  
value 11.4 (2000g) was stirred with aqueous acetic  
solution (800 ml glacial acetic acid diluted to 1000 ml)  
for 1 hr at ambient temperature (25 to 30°C). It was  
10 then allowed to settle and the aqueous layer separated  
(912g).

15           The oil layer was re-extracted with 1000 ml of  
aqueous acetic acid of the above composition and aqueous  
layer separated (990g). The combined extracts (1902g)  
were held at ambient temperature (25-30°C) for 3 days and  
crystals of pongamol were collected by filtration. They  
were washed with hexane (b.p. 65/70°C) 3 x 70 ml and  
dried in vacuum (~5mm) at ambient temperature.

20           The pongamol isolated (18g) was homogenous on tlc  
(hexane:ether:acetic acid 3:1:0.1), had a melting point  
of from 126°C to 127.5°C and UV absorption \ max at 350  
nm; the extinction coefficient  $\epsilon$  was 21,800 and  
25 structural confirmation was done by melting point and  
spectral data.

30           The oil remaining after the separation of aqueous  
acid layer can be washed by stirring with water (2 x 200  
ml) for 30 minutes followed by settling, then similarly  
with saturated brine (2 x 500 ml) at 80°C to free acetic  
acid, and the washed oil recovered (1855 g).

35           This recovered oil so obtained is of higher quality  
than raw karanja oil, and can be used for making good  
quality soap. Hardening of the recovered oil is easier

to achieve, as catalyst consumption is lower than that experienced when raw karanja oil is used.

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CLAIMS

1. A process for the extraction of a diketone which comprises the steps of:

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- i) extracting plant material obtained from Pongamia sp. or from Tephrosia sp. with an organic acid, and
- 10 ii) separating a diketone from the acidic extract so obtained.

2. A process according to claim 1, in which the diketone is Pongamol.

15 3. A process according to claim 1 or 2, in which the plant material is chosen from oil derived from shell, bark, root, stem, seed and mixtures thereof.

20 4. A process according to any of claims 1, 2 or 3, in which the Pongamia sp. is chosen from P. glabra and P. pinnata.

25 5. A process according to claim 1, 2 or 3, in which the Tephrosia sp. is chosen from T. purpurea, T. Hamiltoni, T. flasiformis, T. Vogellii, and T. Lanceolata.

30 6. A process according to any preceding claim, in which the organic acid is aqueous acetic acid.

7. A process according to claim 6, in which the aqueous acetic acid comprises from 65 to 85% w/w acetic acid.

35 8. A process according to any preceding claim, in which separation of the diketone from the acid extract is accomplished via crystallisation.



9. A process according to claim 8, in which the crystallisation of the diketone is directly from the extract.

5 10. A process according to claim 8, in which the crystallisation of the diketone is achieved from an organic solvent solution following removal of the acid used for extraction.

10 11. A process according to claim 10, in which the organic solvent is methanol.

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